A

THESIS

ON

Reactive Extraction of Butyric Acid using Tri-Octyl Amine in Decanol

In partial fulfilment of the requirement for the degree of

MASTER OF TECHNOLOGY

IN

Chemical Engineering

SUBMITTED BY

Miss Deepika Negi

Roll No. 214CH1102

UNDER THE SUPERVISION

OF

Dr. Basudeb Munshi

NATIONAL INSTITUTE OF TECHNOLOGY,

ROURKELA

DEPARTMENT OF CHEMICAL ENGINEERING

May, 2016

Department of Chemical Engineering
National Institute of Technology, Rourkela
CERTIFICATE

This is to certify that **Miss. Deepika Negi** has carried out the project work titled "***Reactive Extraction of Butyric Acid using Tri-Octyl Amine in Decanol***" within the stipulated time. It is hereby approved that the work done by him is a creditable study in the field of chemical engineering and is carried out with all the details and precisions for the fulfilment of the purpose under my supervision and guidance.

Date:

Place: Rourkela

Dr. Basudeb Munshi
Associate Professor
Department of Chemical Engineering
National Institute of Technology
Rourkela

ACKNOWLEDGEMENT

In pursuit of this academic endeavour, I feel that I have been singularly fortunate; inspiration, guidance, direction, co-operation, love and care all came in my way in abundance and it seems almost an impossible task to acknowledge the same in adequate terms. Yes, I shall be failing in my duty if I do not reciprocate my profound sense of indebtedness and heartfelt gratitude to my guide **Dr. Basudeb Munshi** who guided me in pursuance of this work. His association will remain a beacon light to me throughout my career.

I am also thankful to all of my faculties and support of the staff of Department of Chemical Engineering, National Institute of Technology, Rourkela, for their constant help and for extending the departmental facilities for my project work. I would like to extend my sincere thanks to my senior, Sourav Mukherjee for his help in completion of my project. Last but not the least, I wish to profoundly acknowledge my family for their constant support.

Date:

Deepika Negi

Roll No. 214CH1102

ABSTRACT

Reactive extraction is a separation technique using the reaction between extractant and the material to be extracted. The extractant present in the organic phase reacts with the material present in the aqueous phase and the reaction complexes thus formed are solubilized in the organic phase. The application of reactive extraction for separating Butyric Acid (BA) from its aqueous solution is a new technique. Butyric acid (BA, $CH_3CH_2CH_2CO_2H$) also known as butanoic acid, abbreviated as BTA, is a short chain carboxylic acid. It has many important applications in various industries. It can be used as an energy source by converting into butanol by biological conversions. It is anti carcinogenic, as it induces morphological and biochemical differentiation in a range of cells, which leads to concomitant suppression of neoplastic properties and presently it is being used as a precursor to biofuels. It is a promising chemical as it has the potential for future energy needs by converting into butanol through biological transformation. Study of effect of pH on reactive extraction process is essential because pH varies as the process of reactive extraction proceeds. Normally pH of solution containing acid is below pKa values of the respective acid but as the extraction proceeds, due the removal of the acid, pH approaches near 7.0. Thus for reactive extraction process an extractant-diluent combination is required which could recover the acid efficiently at all pHs . Fermentation process usually operates in the temperature range of 305 to 313 K. Thus an extractant is effective only if it operates efficiently in this temperature range. In addition to this, the climate variation, feed and bioreactor conditions makes the study of temperature effect even more important.

Keywords: Reactive extraction, Butyric acid, 1-decanol, Tri-octyl amine, pH, Temperature.

LIST OF FIGURES

LIST OF TABLES

Table of Contents

Nomenclature

Sl. No.	Notation	Meaning
1	[BA]	Initial concentration of butyric acid in gmol/lit
2	E%	Extraction efficiency in percentage (%)
2	$[HA]_{aq}$	Concentration of butyric acid in aqueous phase in gmol/lit
3	$[HA]_{org}$	Concentration of butyric acid in organic phase in gmol/lit
4	k_D	Distribution coefficient
5	$k_D^{diluent}$	Distribution coefficient of diluent alone
6	$k_{E(1:1)}$	Equilibrium complexation constant for 1:1 complex formation in$(gmol/lit)^{-1}$
7	$k_{E(2:1)}$	Equilibrium complexation constant for 2:1 complex formation in$(gmol/lit)^{-1}$
8	TOA	Tri-octyl Amine
9	$[T]_{org}^{0}$	Initial concentration of tri octyl amine in the organic phase $(gmol/lit)^{-1}$
10	z	Loading Ratio
11	z_s	Stiochiometric Loading Ratio

CHAPTER: 1
INTRODUCTION

Petroleum stock is one among the major sources of carboxylic acid. But as the natural reservoirs are depleting and with it their price is also increasing, we need to search for an alternative source of carboxylic acid. Alternatively, fermentation industry is growing at a very fast pace [1]. Carboxylic acids such as propionic, caproic, maleic, succinic, butyric acid are some of the useful products obtained from fermentation industry. But the acid produced is very less, leading to a difficult task for chemical engineers to recover the carboxylic acid from the mixture [5]. The increasing demand for carboxylic acid, focuses our attention towards the improvement of a traditional recovery processes for the production of carboxylic acids. Presently many traditional methods are available for the acid separation from the fermentation broth such as precipitation, liquid extraction, solvent extraction, membrane process, ultra filtration, reverse osmosis, electro-dialysis, distillation, liquid surfactant membrane extraction and anion exchange. But, these methods are not suitable because of their high energy and chemicals demand and also they produce unwanted waste. Separation and purification stages lead to 50% of the production costs. One of the best alternative to recover dilute carboxylic acid is reactive extraction [8].

1.1 Use of reactive extraction process to recover carboxylic acids

Reactive liquid-liquid extraction is a separation technique for the recovery of organic acids, using the reactions between suitable extractants and the materials to be extracted. Reactive extraction is a promising alternative to the conventional processes. Extractant present in the organic phase reacts with the material present in the aqueous phase and the complexes thus formed are solubilized in the organic phase [2]. Extractants such as carbon-bonded oxygen-bearing extractants (also known as inert aliphatic and aromatic hydrocarbons), phosphorus-bonded oxygen-bearing extractants, high-molecular weight aliphatic amines are mostly used in the reactive extraction process of carboxylic acids. Extraction using a specific extractant, which gives a comparatively higher distribution coefficient, is a promising technique for the extraction of carboxylic acids [3].

1.2 Motivations of the present research work

Carboxylic acids are some of the useful products obtained from fermentation industry. But the acid produced is very less, leading to a difficult task for chemical engineers to recover the carboxylic acid from the mixture [5]. The increasing demand for carboxylic acid, focuses our attention towards the improvement of a traditional recovery processes for the production of

carboxylic acids. Reactive liquid-liquid extraction is a separation technique for the recovery of organic acids from their dilute solutions. Optimized process has to be determined for each carboxylic acid. So it is important to study the impact of pH, temperature and stirring on reactive extraction process. Study of effect of pH on reactive extraction process is essential because pH varies as the process of reactive extraction proceeds. Different extractants give different performance at various pH values. Thus for reactive extraction process an extractant-diluent combination is required which could recover the acid efficiently at all pH [22]. Fermentation process usually operates in the temperature range of 305 to 313 K. Thus an extractant is effective, if it operates efficiently in this temperature range. In addition to this, the climate variation, feed and bioreactor conditions makes the study of temperature effect even more important.

1.3 Sources and Applications of Carboxylic Acids

Carboxylic acids are organic acids characterized by carboxyl (–COOH) functional. Carboxylic acid and carboxylic acid compounds have found their applications in food industries, beverage industry (as an acidulate), pharmaceutical industries, surfactants detergents, green solvents and polymers [6-7]. Natural source of carboxylic acids are crude oil reservoirs. But as the natural crude oil reservoirs are vanishing, there is a need for alternative biological production of the acid. Fermentation process is preferred over crude oil reservoirs, due to their increasing cost. Carboxylic acids act as the basic building block for variety of chemicals, thus are used as a starting material in various chemical industries.

Carboxylic acids produced from fermentation processes are recovered from the waste stream and the fermentation broth. Also carboxylic acids are present in dilute form in the waste water stream. Most of the carboxylic acids are produced from carbohydrates or other raw materials by fermentation as, acetic acid which is widely used in food industry is conventionally produced by biological oxidation of ethanol, and is not isolated [18]. Extraction of these dilute solute species is done by reactive extraction. Appropriate combination of extractant, solvent and process conditions are extremely important for the best recovery of the solute.

Though, fermentation process is effective but the final product separation is economically unfavourable, because of the 60-70% of the product cost [6]. However, researchers like Ingale, et. al. (2001) and Fernando, et. al. (2006) have proposed the recovery of carboxylic acids using reactive extraction. Key requirements of a good recovery process are purity, high

extent of recovery, low chemicals and energy demand, low waste byproduct, and modest investment costs.

1.4 Butyric Acid

Carboxylic acids are organic acids with atleast one carboxylic group (-COOH) as acetic acid, propionic acid, butanoic acid, etc. Butyric acid (BA, $CH_3CH_2CH_2CO_2H$) also known as butanoic acid, abbreviated as BTA, is a short chain carboxylic acid. Butyric Acid is a clear colourless liquid with an unpleasant smell, which is soluble in water and many other organic solvents, and has a freezing point at −7.9 °C and boiling point at 163.5 °C. BA is a combustible corrosive liquid, which causes severe skin burns and eye damage. It has many important applications in various industries. It can be used as an energy source by converting into butanol by biological conversions [7-9]. It is anti carcinogenic, as it induces morphological and biochemical differentiation in a range of cells, which leads to concomitant suppression of neoplastic properties and presently it is being used as a precursor to biofuels. It is a promising chemical as it has the potential for future energy needs by converting into butanol through biological transformation. Butyric acid is also used in the manufacturing butyrate esters. These esters of butyric acid, such as methyl butyrate, have pleasant aromas or tastes, thus are used as food and perfume additives. It is also used as a supplement for animal feed, because of its ability to reduce pathogenic bacterial colonization. Because of its wide range of applications researchers have focused on the reactive extraction of butyric acid from fermentation broth. Biosynthetic production of BA for such purposes is preferred. In fermentative production of butyric acid, strong biosynthesis inhibition by the product occurs [11-14]. Possible solution of this problem lies in the separation of BA from the fermentation solution by extraction. Extractive separations of BA from low concentration solutions by classical solvents with reactive extractants, e.g. tri-alkyl amines, TBP or others, diluted by hydrocarbons or alcohols have been widely studied by several authors [20]. However, tertiary amines offer advantages over other extractants because of their low cost, low solubility in water, good regenerability and high distribution coefficient, K_D. Tertiary amines were found effective in the extraction of lactic acid using alcohol as diluent. Using alcohol as diluent bestowed another advantage of formation of acidic ester which could be easily separated.

1.5 Reactive Extraction

Reactive extraction strongly depends on various parameters such as the distribution coefficient, degree of extraction, loading ratio, complexation equilibrium constant, types of complexes (1:1, 2:1, etc.), rate constant of carboxylic acid-extractant reaction, properties of the solvent (extractant and diluent), type of solvent, temperature, pH and acid concentration[17-19].

Reactive extraction comes under advanced separation processes, and is used to intensify separation. Process intensification occurs by solvent extraction i.e. by reaction between the chemicals (solute and extractant reaction) and by physical phenomena i.e. by diffusion and solubilization of the components. As there is no heat transfer in the extraction process, so it is found to be very much energy efficient. It links the two main parameters of any chemical industry *viz.* the conversion and selectivity [21].

Reactive extraction is found to be a promising alternative to the conventional processes, but one has to optimize the process for the economic recovery of organic acids. The efficiency of the reactive extraction process depends on various parameters as distribution coefficient (k_D), extraction efficiency (E%), loading ratio(z), stiochiometric loading ratio(z_s), complexation equilibrium constant(k_E), types of complex formed (1:1, 2:1, 3:1, etc.) [16]. Acid and the extractant together form a complex which is separated against the other non-acidic components. Diluents help in the solvation of the extractants, as extractants are viscous in nature. Also, diluents improve the physical properties of the extractant. Most commonly used diluents are alcohols, ketones, esters, etc.

Extraction of a specific carboxylic acid uses specific extractant, the choice of the extractant depends on its distribution coefficient. Higher the distribution coefficient better will be the extractant. pH is a vital parameter in fermentation broth [22]. Reactive extraction has an important advantage of easy removal of the acid produced from the fermentation broth, thereby preventing the lowering of the pH. As extractant is quite expensive, it should be reversible in nature. On successful separation of the acid from the complex formed, extractant is recycled to the fermentation process. This reversible nature of the extractant makes the reactive liquid-liquid extraction process economical. Reactive liquid-liquid extraction process is advantageous over other methods because of its higher productivity, pH control without

base addition, Usage of a high-concentration substrate as a process feed to decrease down the process waste and production cost, produce[14].

1.5.1 Merits and Demerits of Reactive Extraction

Merits of reactive extraction are as follows:

1) The most significant advantage is the separation of elements from the dilute solutions.
2) Solvent extraction allows separation of element in two different oxidation states.
3) The flexibility of adjustment of pH or controlling reagent concentration or choice of diluents or organic carboxylic acids facilitated the selective separation of large number of elements.
4) Further purification is not required because the product obtained is already in pure form.

Demerits of reactive extraction are as follows:

1) Formation of third phase during extraction.
2) If extraction of acid is carried out from bioreactors, the toxicity of the solvent system is matter of concern [7].

1.5.2 Physical and Chemical Extraction

1.5.2.1 Physical Extraction

In physical extraction solute is extracted into inert non reacting hydrocarbons and substituted hydrocarbons and is comparatively free of complexities. Physical extraction by natural diluents, aliphatic and aromatic hydrocarbons is very poor. These are apolar aprotic solvents and are unable to act as a hydrogen bond donor [9].

Following factors are to be considered for physical extraction:

1) Acid ionization in the aqueous phase.
2) Partial dissociation of the acids between the two phases.
3) Dimerization in the organic phase.

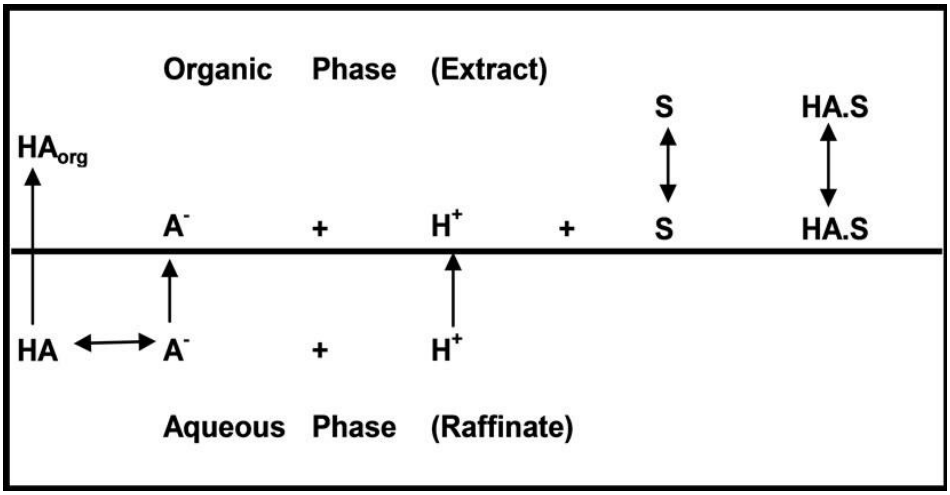

Figure 1.1: Physical extraction of mono carboxylic acid

1.5.2.2 Chemical Extraction

It involves mixture contact with a second phase which consists of extractant that reacts reversibly with the solute. Extractant to be used depends on its strong, specific and reversible reaction with the solute. Because of the viscous nature of the extractant, it is dissolved in low viscosity diluents. Diluent improves the equilibrium by solvation of the complexes and can also affect the process in other ways [9].

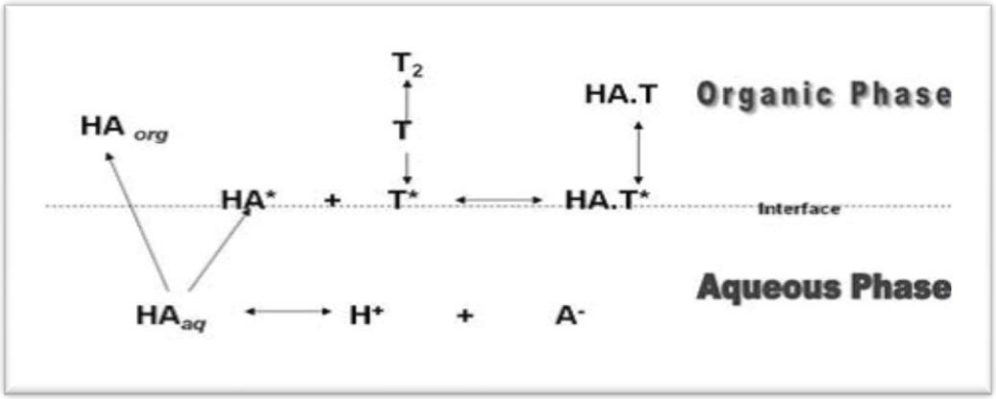

Figure 1.2: Chemical extraction of mono carboxylic acid

There are three main types of extractants are as follows:

(1) Conventional oxygen-bearing and hydrocarbon solvents: These give relatively low distribution coefficient, example ketones, acetones, etc.

(2) Phosphorous bonded oxygen bearing extractants: organophosphates, such as tri-*n*-butyl phosphate and trioctyl phosphine oxide compounds which involves solvation of the acid by donor bonds, which are different from strong covalent bonds and form ionic interactions. These give relatively higher distribution coefficient.

(3) High molecular weight aliphatic amines: These involve aproton transfer or ion-pair formation reaction, example trioctylamine, etc.

High molecular weight aliphatic amines are found to be more effective and cost efficient than the organophosphorous compounds. Aliphatic amines (such as, tri-n-octyl amine (TOA), Aliquat 336, Alamine 336 etc.) are widely used for the extraction of carboxylic acids like acetic, caproic, pyruvic, butyric and propionic [8]

Extractant used in the reactive extraction process, should possess the following properties:

1) Low viscosity.
2) Higher density difference between the extractant and the raffinate.
3) A medium interfacial tension.
4) Thermal stability.
5) Low enthalpy of vaporization.
6) Low melting point.
7) No reaction between the extractant and the raffinate.
8) Low solubility of the extractant in the raffinate.
9) Low toxicity and good biological degradability.
10) Low price and good availability.

To improve the extraction ability of extractant, extractants are dissolved in diluents. Diluents also affect the physical properties of the extractant e.g. improving their viscosity, etc. Two factors are needed to account the influence of diluents on the extraction process:

A) Partial dissociation of solute in the aqueous phase

B) Dimerization in the hydrocarbon phase.

Another important parameter is the water of hydration. For the extraction of carboxylic acid, high attraction of binding of the acid with the water molecule requires large amount of solvent molecules so that they can compete with the water molecule that hydrates the acid at the interface [17].

1.6 Effect of pH on Reactive Extraction Process

Study of effect of pH on reactive extraction process is essential because pH varies as the process of reactive extraction proceeds. Normally pH of solution containing acid is below pKa values of the respective acid but as the extraction proceeds, due the removal of the acid, pH approaches near 7.0. Thus for reactive extraction process an extractant-diluent combination is required which could recover the acid efficiently at all pH [22].

Different extractants give different performance at various pH values. Tertiary amines and organophosphorous compound are found to extract the acid in undissociated form. With the increase in the pH of the system, the fraction of dissociated forms increases over the undissociated form and hence these extractant perform poorly in neutral and basic media.

Quaternary amine such as Aliquat 336 is unaffected with the pH of the system and extracts all the forms. Thus pH is maintained in 6-7 range throughout.

1.7 Effect of Temperature on Reactive Extraction Process

Fermentation process usually operates in the temperature range of 305 to 313 K. Thus an extractant is effective, if it operates efficiently in this temperature range. In addition to this, the climate variation, feed and bioreactor conditions makes the study of temperature effect even more important. Effect of temperature is attributed to the effect of different parameters like the acids pKa, the extractant-acid interaction, and the solubility of the acid in both the phases, the extractant basicity and water coextraction. These parameters were studied by Canari and Eyal (2004).They concluded that the pKa values of common carboxylic acids decreases only slightly when the temperature is increased. Similarly pKa measurements for carboxylic acid is an exothermic process and with the increasing temperature, the extractant efficiency decreases. However, it can be stated that the decrease in extraction is also a exhibits a small decrease when the temperature is increased but only up to a given point. Above it the pKa value increases [18]. Similarly solubility of the acids is affected by the

temperature in both the aqueous and extractant phase. Higher the negative value of ΔH for a particular acid suggests that more exothermic will be the extraction. This may be accounted due to the difference in the partial molar heat of mixing of the acid in the aqueous phase. Mostly, extraction decreases by around 50% with increase in the temperature.

1.8 Research Objectives

The main objectives of the present research work are stated below:

I. Effect of temperature and pH on the reactive extraction of butyric acid.
II. Determination of distribution coefficient (k_D), extraction efficiency (E %), loading ratio (z) and stiochiometric loading ratio (z_s) for the acid-extractant-diluent system.
III. Determination of the equilibrium complexation constant (k_E), ΔH, ΔS and the type of complex formed by the acid-extractant system.

1.9 Organization of the Thesis

Thesis consists of five chapters namely Introduction, Literature Review, Materials and methods, Results and Discussion and Conclusions. Each chapter completely details the past and the present research in the field, experimental techniques used, research conclusion and their possible explanations.

Chapter 1: Introduces the source of carboxylic acid, fermentation technology, idea of reactive extraction, objectives of the present research work and thesis overview.

Chapter 2: It lists the past work pertaining to the reactive extraction of carboxylic acid and other related parameters, which affect the equilibrium and kinetics of the process. Both national and international works related to reactive extraction are discussed. A wide range of acid-extractant-diluent systems are elaborated.

Chapter 3: It describes the experimental methods and set up used in the present research work.

Chapter 4: It consists of the results obtained from the experiments and their expected explanations.

Chapter 5: Summary of the overall work done and conclusion drawn from the results and observation during this study.

Chapter 6: It deals with the future work which could be carried out related to the current project.

CHAPTER: 2
LITERATURE REVIEW

Research in the field of reactive extraction of carboxylic acids is going on from1990s. Some of the research work related to the present study has been summarized here.

2.1 Study of the Effect of pH on Reactive Extraction Process

- Yang, et al, (1990) studied the reactive extraction of carboxylic acids by using tertiary and quaternary amines. They concluded that the quaternary amines (Aliquat 336) extracted both dissociated as well as undissociated acids. Whereas only undissociated form of the acid was extracted by the tertiary amine (Alamine 336). Thus quaternary amines can be used under both acidic and basic conditions. Whereas tertiary amines are not efficient at higher pH.

- Eyal and Canari (1995) have investigated the effect of pKa of the amine based extractant on the degree of extraction. Extraction of various acids using various amines based on their strength (strong or weak) has been studied with taking into consideration the effect of pH.

- Ingale and Mahajani, (1996), studied the effect of pH, salts on reactive extraction of butyric, valeric and caproic acid by TBP. Existence of mineral acid with its salt had a profound effect on the extraction efficiency of TBP. Complex NaCl-HCl system was found to have more effect on k_D**,** than H_2SO_4, Na_2SO_4 system alone.

- Kahya, et al, (2000), found out that when Alamine 336 diluted with oleyl alcohol used as the solvent, the extraction efficiency was increased. The effects of initial lactic acid concentration, pH, temperature, extraction time, stirring rate, the amount of Alamine 336 in oleyl alcohol and the ratio of organic phase volume to aqueous phase volume, V_{org}/V_{aq}, on the distribution coefficient of the lactic acid, K_D, were investigated. K_D increased with increasing stirring rate, extraction time and amount of Alamine 336 and V_{org}/ V_{aq}, and decreased with increasing temperature and initial lactic acid concentration. Optimum conditions for reactive extraction of the lactic acid were determined by using the Linear Box-Wilson experimental design method.

- Hong, et al, (2001), studied the Effect of pH on the reactive extraction of succinic and formic acids using Tri-n-octylamine and 1-octanol. Sharp decrease in the loading ratio

at different pH was observed according to the pKa values of each acid. Bisuccinate anion formation plays a vital role in the stoichiometry of the complex.

- Hong, et al (2001) studied the Applications and challenges of Reactive Extraction process to the recovery of Carboxylic Acids. Among other recovery processes, reactive extraction was found to be the most efficient process. Fermentation with reactive extraction yields high productivity. Presently solid sorbents having tertiary amine as functional group are promising. For higher separation, one must overcome pH limitation. Carboxylic acids have a wide range of industrial applications.

- Li et al (2002) studied the extraction equilibrium of monocarboxylic acid by TOA and TRPO and found that the apparent extraction equilibrium constant of 1:1 complex $k_{E(1:1)}$ was found with the help of log P and pKa.

- Hong, et al, (2005) studied the Removal of acetic acid from aqueous solutions of succinic and acetic acid using tri-n-octylamine, under wide range of pH of aqueous solutions. For both the acids, loading ratio decreases with increase in pH. For acetic acid, sharp decrease in the loading ratio with increase in pH was observed at higher values compared to succinic acid extraction because of its higher pKa value. Also extraction using Tri-octylamine in 1-octanol was decreasing with increase in pH of aqueous phase. If amine extractants are used in reactive extraction fermentation process for succinic acid, the pH effect on acid extractability becomes important.

- Shan, et al, (2006), described the extraction equilibrium of monocarboxylic acids from aqueous solutions. Three main factors were found to influence the extraction equilibrium of carboxylic acids from aqueous solutions, namely the acid hydrophobicity (log P), the dissociation equilibrium constant of the acid (pKa) and the apparent basicity of the extractant to HCl.

- Kumar and Babu, (2009), researched on the recovery of nicotinic acid from enzymatic production by reactive extraction was carried out. The enzymatic production of nicotinic acid was intensified by its recovery from the fermentation broth by implementing reactive extraction.

- Oliveira, et al, (2012), studied the extraction of lactic, malic and succinic acids using phosphonium-based ionic liquids. Anion's nature and the acid concentration affected the partition coefficient. Reduced pressure distillation approach and pH variation approach were used to recover the carboxylic acid. It was concluded that the phosphonium-based ILs are better extractants than the conventional organic solvents.

- Wasewar and Shinde, (2011), studied the recovery of caproic acid from the aqueous waste stream by using Aliquat-336 in two diluents MIBK and Xylene was carried out. Equilibrium parameters were evaluated for the process. In another study extraction of caproic acid using tri-butyl phosphate (TBP) in hexanol, octanol and decanol was performed. Four different models, relative basicity, mass action law, Langmuir, and linear solvation energy relationship (LSER) models, were used to represent the reactive extraction equilibrium for caproic acid-TBP-diluent.

2.2 Study of Effect of Temperature on Reactive Extraction Process

Study of effect of temperature is vital from the point of view of operating temperatures and back-extraction (regeneration steps).

- Riki Canari and Aharon M. Eyal Casali (2004) studied the reactive extraction of carboxylic acids by lipophilic amines extractants and their dependency on temperature. Profound effect of temperature effects was observed by using relatively weak alkyl amine. Strong temperature effectwas observed for systems having weak ion pair interaction between the protonated amine and the anion of the acid.

- Amit Keshav, et al, (2009), studied the extraction of monocarboxylic acids *viz.*acrylic, and propionic by Aliquat 336 in oleyl alcohol and thereby studied the effect of temperature for a temperature range of 305-333K. They calculated the effect of temperature on the partition coefficient. Enthalpy and entropy of the system was determined at different temperatures.

- Keshav and Wasewar (2010) described various methods of back extraction *viz*. NaOH back extraction, trimethyl amine, temperature and diluent swing. Back extraction using NaOH and trimethyl amine have higher solubility of the carboxylic acids in these substances in comparison to organic phase. Temperature and diluent

swing extraction is based on the changes in the extraction equilibrium. 100 % regeneration is obtained using NaOH and trimethyl amine extractions.

- Tamada and King (2010) studied the reactive extraction for succinic and lactic acids by Alamine 336 in methyl-isobutyl ketone (MIBK) and chloroform. It was observed that the extraction decreases with increase in the temperature. Enthalpies were more negative, i.e. exothermic for succinic acid than for the lactic acid and also more exothermic in chloroform than in the MIBK. Entropy decrease was observed to be higher for succinic acid than for lactic acid and also higher in chloroform than in MIBK. 1:1 complexes were more exothermic and had higher loss of entropy than 2:1 and 3:1 complexes.

- Harington and Hossain (2012) studied the reactive extraction of lactic acid by TOA dissolved in sunflower oil. It was observed that with increase in temperature, distribution coefficient (k_D) increases. As the optimal temperature of fermentation broths is around 38 °C, therefore, extraction near this temperature allows higher extraction than at room temperature.

- Hasan Uslum and S. Ismail Kirbaslar (2013) studied the effect of temperature and initial acid concentration on the reactive extraction of levulinic acid and malic acid. Experiments were performed at the temperatures 298 K, 318 K and 328 K and results showed that with increase in temperature, distribution coefficients (k_D) decreases. Reactive extraction was found to be exothermic because of the negative values of enthalpy. Distribution coefficients decreases with increase in initial concentration of acids (0.08 wt % to 0.15 wt %).

CHAPTER: 3

MATERIALS AND METHODS

3.1 Materials

BA (Otto), 1-decanol (Loba Chemie) were of reagent grade and TOA (Merck, 95%, Density-0.816 g/ml, Solubility in water-0.2 g/lit) was of analytical grade. Aqueous phase was prepared by dissolving BA in distilled water. For experiments BA concentration was kept low because practically the concentration of butyric acid in fermentation industry is very low. NaOH of laboratory grade was used for titration. Oxalic acid was used for the standardization of NaOH. Phenolphthalein solution (pH-8.2 to 10.0) was used as an indicator. Trioctyl Amine concentrations in decanol were varied from 0% to 10% on volume by volume basis.

Table 3.1: **List of Chemicals used in the present work**

Sl. No.	Name of the Chemical	Manufacturing Company	Properties at 25^{o}C
1	Butyric Acid	Otto	Density-0.958 g/cm^3
2	1-Decanol	Loba chemie	Density-0.8297g/cm^3
3	Tri-Octyl Amine (95%)	Merck Specialities	Density-0.816g/ml
4	NaOH Pellets	Fisher Scientific	Assay-95%
5	H_2SO_4	Loba Chemie	Density-1.840 g/ml
6	HCl	Loba Chemie	Density- 1.017 g/ml
5	Oxalic Acid Pellets	Fisher Scientific	Assay-98%
7	Phenolphthalein	Loba Chemie	pH - 8.3 to 10

3.2 Methods

3.2.1 Equilibrium Study

Experiments were carried out at atmospheric pressure and at a temperature range of 25-45^{0}C.

1. **Preparation of stock (aqueous phase) solution:** The aqueous phase solution is prepared by mixing butyric acid in distilled water. For studying the effect of pH, aqueous phase pH is varied by adding HCl and H_2SO_4.
2. **Preparation of organic phase solution:** Tri-octyl amine as extractant and 1-decanol as diluent are mixed together in different volume by volume ratio, so as to make 10ml organic phase solution.

3. **Mixing of aqueous phase and organic phase solutions:** The two phases being immiscible are mixed in an incubator shaker for 8 hours. For studying the effect of temperature, the incubator shaker temperature is varied from 25^{o}C to 45^{o}C
4. **Separation of the aqueous and organic phase:** After mixing, once the equilibrium is achieved the solution mixture is poured down into the separating funnel. The two phases are then allowed to settle down for at least 2 hours. Aqueous phase being heavier in density settles below organic phase.
5. **Determining the pH of aqueous and organic phase solution:** pH of the both, aqueous and organic phase solutions are determined using pH meter.
6. **Calculating the acid content of the aqueous phase:** Aqueous phase acid concentration is determined with the help of titration. NaOH solution is used for the titration of the aqueous phase solution. Furthermore, standardization of the NaOH solution is done by using fresh Oxalic acid solution. Phenolphthalein is used as an indicator. Light baby pink colour of the aqueous phase indicates the end point of the titration.

   Following equation holds for neutral solutions:

   $$N_1V_1=N_2V_2 \quad (1)$$

   Where,

   N_1: Normality of titrant

   N_2: Normality of titrate

   V_1: Volume of titrant

   V_2: Volume of titrate

   N_1 is calculated for the known values of V_1, N_2 and V_2.
7. **Calculating the acid content of the organic phase:** Acid content of the organic phase is calculated by using mass balance relation. For cross checking the results, UV Spectroscopy of the organic phase is also carried out.
8. **Calculating the distribution coefficient (k_D) value:** Distribution coefficient is determined using the following formula:

   $$k_D = \frac{[HA]org}{[HA]aq} \quad (2)$$

   Where, $[A]_{org}$= Concentration of the acid in the organic phase.

   $[A]_{aq}$= Concentration of the acid in the aqueous phase.

9. **Calculating the extraction efficiency (E%):** The extraction efficiency is determined using the following formula:

$$E\% = \frac{k_D}{1+k_D} * 100 \quad (3)$$

10. **Calculating the loading ratio(z):** The extent to which Tri-octyl amine + 1-decanol can be loaded with the butyric acid is expressed in terms of loading ratio, z:

$$z = \frac{[HA]_{org}}{[T]^0_{org}} \quad (4)$$

Where,

$[HA]_{org}$ = Acid concentration in the organic phase after extraction.

$[T]^0_{org}$ = Tri-octyl amine concentration in the organic phase before extraction.

11. **Calculating Stiochiometric Loading Ratio/ Factor (z_s):** is defined as the ratio of the acid concentration in the organic phase complexed with Tri-octyl amine alone to the initial concentration of tri-octyl amine. This factor includes a correction term $v[HA]^{diluent}_{org}$, for the amount of acid extracted by the diluent in the solvent mixture.

$$z_S = \frac{[HA]_{org} - v[HA]^{diluent}_{org}}{[T]^0_{org}} \quad (5)$$

Where,

$[HA]^{diluent}_{org}$ **:** Acid concentration in the organic phase after extracted by the diluent alone

*v***:** Ratio of volumes of TOA and 1-decanol

12. **Calculating equilibrium complexation constant (k_E):**

For loading ratios below 0.5 i.e. z<0.5, (1:1) complex of BA and TOA is formed and the following equation is used:

$$\frac{z}{(1-z)} = k_{E(1:1)} * [HA]_{aq} \quad (6)$$

For loading ratio value above 0.5, i.e. z>0.5, (2:1) complex is formed and the following equation is used:

$$\frac{z}{(2-z)} = k_{E(2:1)} * [HA]^2_{aq} \quad (7)$$

Equilibrium complexation constant $K_{E(1:1)}$ and $K_{E(2:1)}$ are obtained from the slope of the graph of z/(1-z) versus $[HA]_{aq}$ for 1:1 complex, and z/(2-z) versus $[HA]^2_{aq}$ for 2:1 complex.

13. **Calculating Enthalpy(ΔH) and Entropy(ΔS):**

If enthalpy and entropy are constant for a given temperature range, then the following Van't Hoff equation holds:

$$\ln(k_E) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

k_E: Equilibrium complexation constant

ΔH: Enthalpy of the reaction

ΔS: Entropy of the reaction

3.3 UV-Visible Spectrophotometer

For measuring concentration of different phases, UV-Visible spectroscopy method was used (JASCO V-750 model). pH measurements of aqueous phases were carried out by pH meter (Hanna, USA).

For measuring concentration of different phases, UV-Visible spectroscopy method was used. Samples (5ml) from the each organic phase were taken periodically from and analysed using UV-Visible spectroscopy.

The concentration is measured with UV-Vis spectroscopy using the Beer-Lambert law, which states that: when a beam of monochromatic light is passed through a solution of an absorbing

substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution.

The expression of Beer-Lambert law is:

$$A = \log (I_0/I) = \mathcal{E} \times c \times l \quad (9)$$

Where, A = Absorbance

I_0 = Intensity of light incident upon sample cell

I = Intensity of light leaving sample cell

C = Molar concentration of solute

L = Length of sample cell (cm.)

Ɛ = Molar absorptivity

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy.

Firstly calibration curve is established with known concentrations 0.1M, 0.2M, 0.3M, 0.4Mand 0.5M butyric acid in 1-decanol. The calibration curves obtained of determination of acid content in the organic phase can be seen in Figure 3.1.

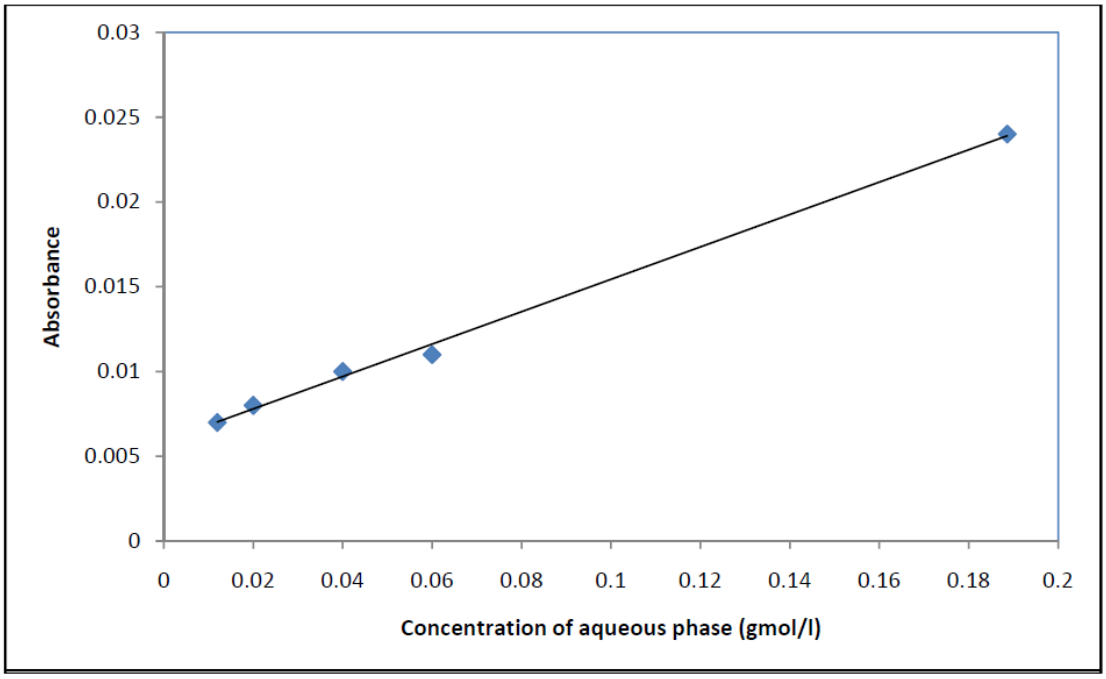

Figure: 3.1: Calibration Curve for the Determination of Acid Content in the Organic Phase

Concentration of samples was found by comparing their UV absorbance with calibration curve.

Figure: 3.2: Sample Kept Over Digital Magnetic Stirrer cum Heater

Fig: 3.3: Sample Tubes Containing Distinct Organic Phase and Aqueous Phase

CHAPTER: 4
RESULTS AND DISCUSSIONS

4.1 Extraction Equilibria

Butyric acid (HA) is a monocarboxylic acid and TOA is a tertiary amine. So the following mechanism occurs between the solute and the extractant:

$$[R_3N]_{(org)} + [HA]_{(aq)} \leftrightarrow [R_3NH^+A^-]_{(org)} \quad (10)$$

Above mechanism is the amine-based extraction of carboxylic acid.

Assumptions taken in the present research work are as follows:

1) Solubility of TOA in the aqueous phase is negligible.

2) TOA reacts only with the undissociated form of the acid.

Following reactions explain the equilibrium of amine-based extraction, which is based on the mass action law.

Carboxylic acids exist in the form of dimers in the organic phase because of the intermolecular hydrogen bonding. Based on above assumptions, the following reactions hold:

$$HA + R_3N \leftrightarrow HA–R_3N \quad (11)$$

$$2HA + R_3N \leftrightarrow (HA)_2– R_3N \quad (12)$$

4.2 Effect of pH

Since the pH of the fermentation broth varies with the acid production, it becomes important to study the effect of pH on reactive extraction of Butyric acid.

Table 4.1: Extraction of Butyric Acid Using 10% TOA in 1-Decanol at 306 K

Initial pH	$[HA]_{org}$	$[HA]_{aq}$	k_D
1.666	0.193	0.007	27.6
2.223	0.192	0.008	24
2.784	0.19	0.009	21.1
3.556	0.184	0.011	17.18
5.62	0.169	0.034	5.63

pH of the dilute 0.2M aqueous phase solution is varied by using H_2SO_4. The above experiment was performed at room temperature. Results show that with increase in pH distribution coefficient decreases.

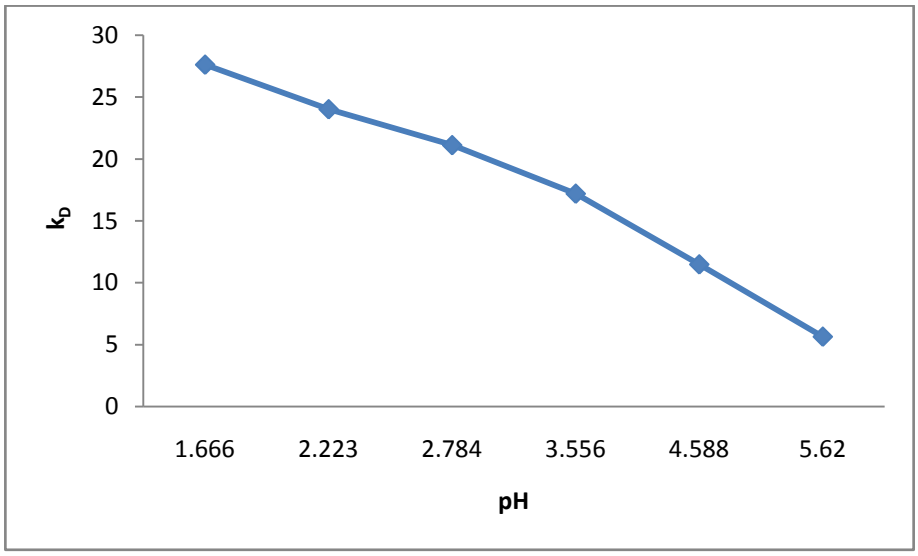

Figure 4.1: Effect of pH on Distribution Coefficient (k_D) of 0.2 M Butyric acid at 306K

Reversible complexation is driven by the amount of un-ionized acid in the solution and is thus favored at a low pH. The optimal pH for separation by complexation is related to the pKa of the acid. Feed solutions with a low pH can have the disadvantage of promoting the extraction of other competing acids in multiple acid systems. At high pH values, where the acid is mostly dissociated, ion exchange is more favorable.

4.3 Effect of pH on Loading Ratio (z) and Stiochiometric Loading Ratio (z_s)

Loading ratio considers the amount of acid extracted by the extractant as well as the diluent. Whereas stiochiometric loading ratio does not takes into account the acid extracted by the diluent. Thus in order to find out the values of stiochiometric loading ratio, two set of experiments were performed for the same pH of the aqueous phase. For one set of experiment organic phase had mixture of both TOA and 1-decanol, and for the other set organic phase had 1-decanol alone.

Table: 4.2: Reactive Extraction of 0.2 M BA Using 10% TOA in 1-Decanol at 306 K

pH	**$[HA]_{aq}$**	**$[HA]_{org}$**	**k_D**	**E%**	**z**
1.41	0.008	0.192	24	96	0.8384
1.71	0.008	0.191	23.87	95.98	0.8341
2.03	0.009	0.191	21.22	95.5	0.8340
2.29	0.009	0.19	21.11	95.47	0.8297
3.38	0.011	0.189	17.18	94.5	0.825
3.64	0.012	0.188	15.67	94	0.8210
4.66	0.016	0.183	11.44	91.96	0.799
5.23	0.024	0.176	7.33	88	0.768
6.08	0.034	0.166	4.88	82.99	0.725

It is a well known fact that the value of pKa is affected by ionic strength of solution. By having higher ionic strength and higher $[H^+]$ i.e. by adding mineral acid externally to aqueous solution, the dissociation of acid will be suppressed. Thereby, the solution will have a larger amount of undissociated acid in aqueous solutions. This effect results in an increase in k_D value. k_D =24 and E =96% values were obtained at a lower of pH=1.41.

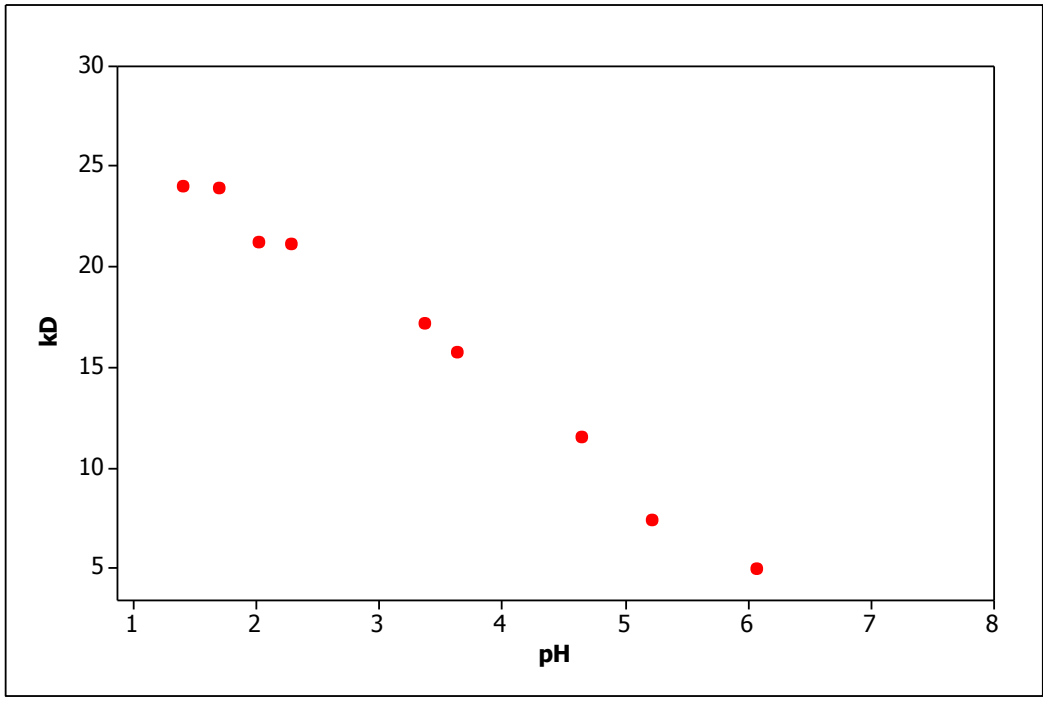

Figure 4.2: Effect of pH on Distribution Coefficient (k_D) of 0.2 M BA at 306K

Figure 4.2 shows extraction of 0.2M butyric acid using TOA. Here pH is varied from 1.41 to 6.08. Results are in agreement with the discussion above. For extraction using TOA, initially as pH is increased from 1.41 to 2.29, there is a gradual decrease in extraction and at higher pH greater than 4, very low k_D was obtained. Thus at pH > pKa of the acid, extraction is very low. Figure 4.2 depicts that the distribution coefficient decreases with increase in pH. This occurs due to the fact that tertiary amines (TOA) are able to extract the acid in there undissociated forms only. H_2SO_4 being stronger acid than BA, H_2SO_4 dissociates into $[H]^+$ and $[SO_4]^{-2}$ and as a weaker acid BA remains in undissociated form. TOA being tertiary amine, extracts BA in its undissociated form. Therefore the distribution coefficient (k_D) decreases with increase in pH. Whereas NaOH dissociates into Na^+ and OH^- ions and hence [HA] dissociates into $[H]^+$ and $[A]^-$ ions, $[H]^+$ and $[OH]^-$ combine together to form water and $[A]^-$ and $[Na]^+$ form butyrate salt and thus k_D decreases with addition of NaOH.

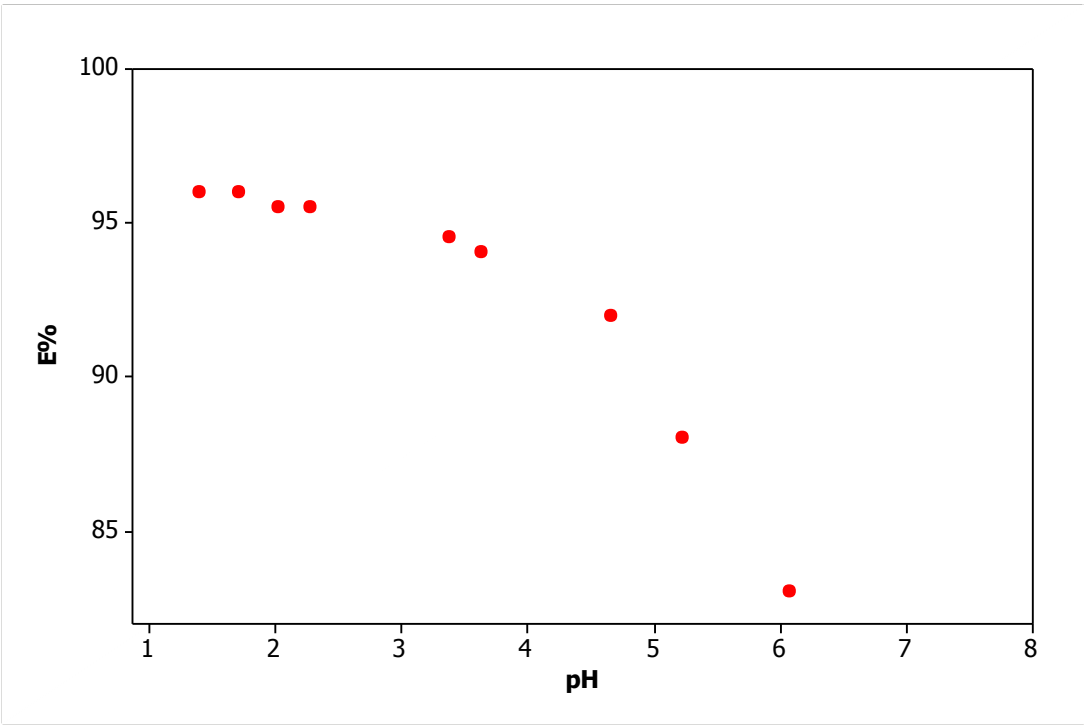

Figure 4.3: Effect of pH on Extraction Efficiency (E %) of 0.2 M BA

We can see that extraction efficiency has decreased from 96% to 82.99%. The reason being that with increase in pH fraction of dissociated forms increases over the undissociated forms and hence tertiary amine perform poorly in neutral and basic media.

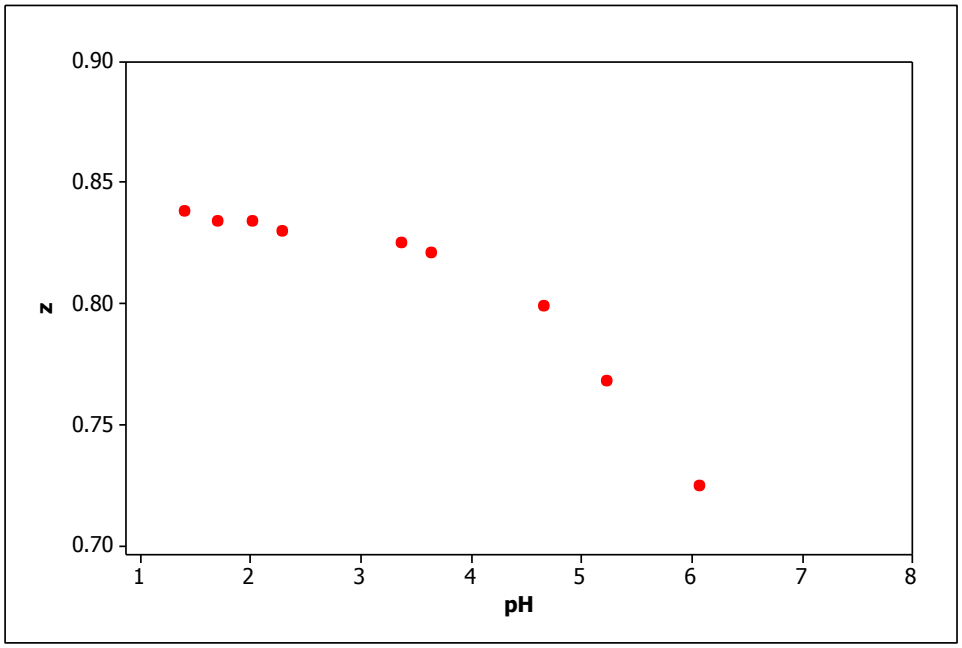

Figure 4.4: Effect of pH on Loading Ratio(z) of 0.2 M BA at 306K.

Loading ratio value determines the extent to which the organic phase (TOA + 1-decanol) can be loaded with the butyric acid present in the aqueous solution. High loading ratio value of 0.8384 indicates the presence of 2:1 complex of butyric acid, tr-octyl amine and 1-decanol. Here also due to the poor transfer of [HA] from the aqueous phase to the organic phase the loading ratio decreases monotonically with pH. Moreover the loading value appears as more than 0.5 which shows the possibility of formation of 2:1 complex.

Table: 4.3: Reactive Extraction of 0.2M BA Using Decanol Alone at 306 K

pH	$[HA]_{aq}^{diluent}$	$[HA]_{org}^{diluent}$	z_s	$k_D^{diluent}$
1.41	0.162	0.038	0.7642	0.234
1.71	0.163	0.037	0.7600	0.227
2.03	0.164	0.036	0.7539	0.228
2.29	0.166	0.034	0.7538	0.22
3.38	0.168	0.032	0.75	0.201
3.64	0.168	0.032	0.725	0.2
4.66	0.166	0.034	0.736	0.2
5.23	0.114	0.086	0.645	0.19
6.08	0.185	0.015	0.696	0.081

Here experiments were performed without tri-octyl amine. We can observe that the value of distribution coefficient decreased down significantly. When diluent alone was used, pH variation did not have much effect on the distruibution coefficient.

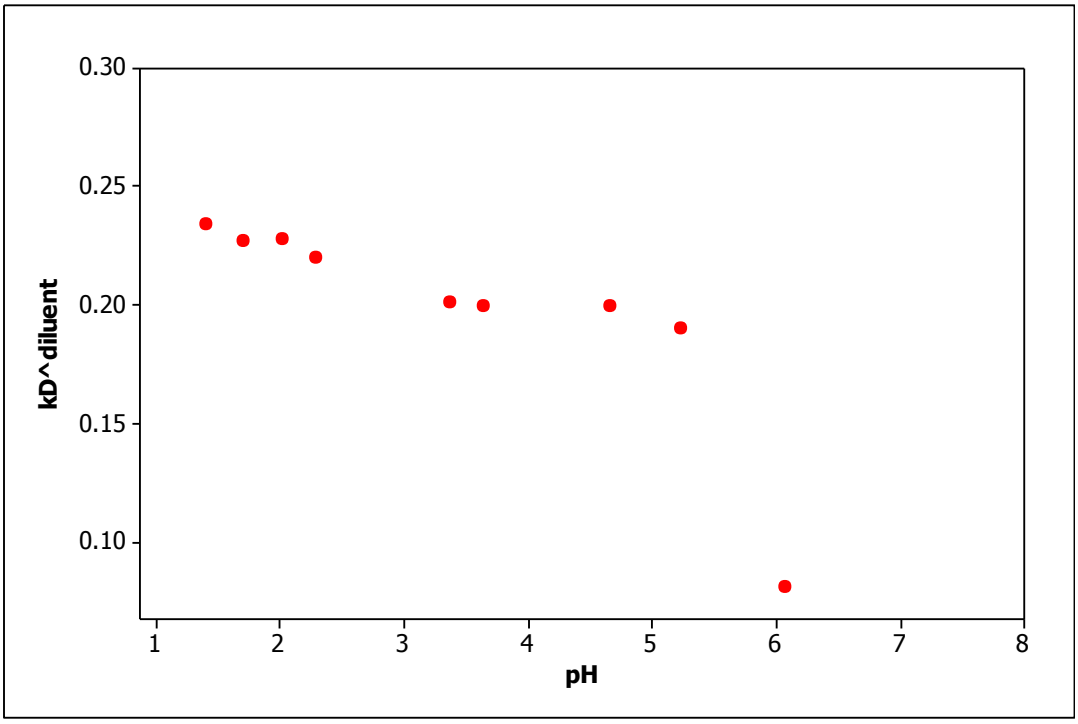

Figure 4.5: Effect of pH on Diluent Distribution Coefficient ($k_D^{diluent}$) at 306K

pH variation did not have much effect on the distribution coefficient of butyric acid. And the same trend of decrease in distribution coefficient with increase in the value of pH is observed

.

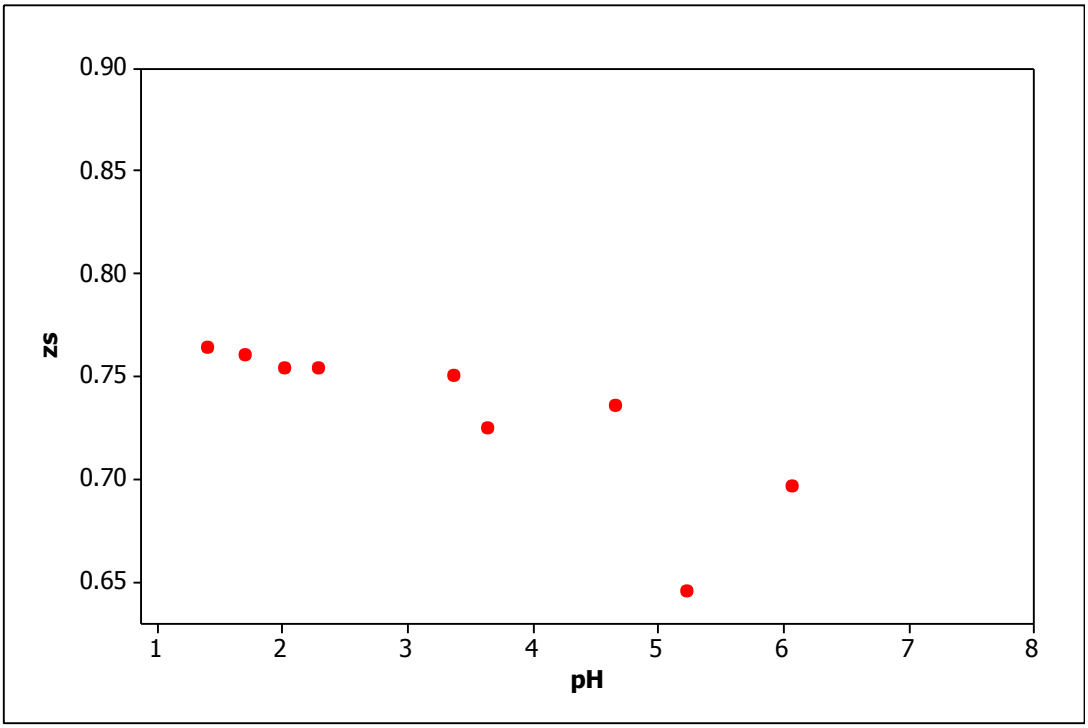

Figure 4.6: Effect of pH on Stiochiometric Loading Ratio (z_s) at 306K

The stoichiometric loading factor z_s, is the ratio of the overall complexed acid to total TOA in the organic phase. This factor includes a correction term$[HA]_{org}^{diluent}$, for the amount of acid extracted by the diluent in the solvent mixture.

$$z_s = \frac{[HA]org - [HA]_{org}^{diluent}}{[T]0\ org} \qquad (13)$$

4.4 Determination of Equilibrium Complexation Constant k_E

The effect of temperature is an important matter of investigation in the reactive extraction processes in view of operating temperatures and back-extraction/regeneration steps.

Table: 4.4: Reactive Extraction of BA Using 10% TOA in 1-Decanol at 301K

[BA]	$[HA]_{aq}$	$[HA]_{org}$	k_D	z	z/(1-z)
0.01	0.002016	0.00798	3.96	0.03486	0.07612
0.03	0.00338	0.02661	7.85	0.1162	0.2014
0.05	0.00475	0.04524	9.51	0.1975	0.2462
0.07	0.0063	0.06369	10.11	0.2781	0.3853
0.09	0.00712	0.08287	11.63	0.3618	0.5671

Table 4.5: Reactive Extraction of BA Using 10% TOA in 1-Decanol at 303 K

[BA]	$[HA]_{aq}$	$[HA]_{org}$	k_D	z	z/(1-z)
0.01	0.00215	0.00784	3.64	0.03423	0.0654
0.03	0.0040	0.0259	6.43	0.1131	0.1775
0.05	0.0050	0.04496	8.92	0.1963	0.2442
0.07	0.00644	0.06355	9.86	0.2775	0.3841
0.09	0.00816	0.08183	10.02	0.3573	0.5559

Table 4.6: Reactive Extraction of BA Using 10% TOA in Decanol at 308 K

[BA]	$[HA]_{aq}$	$[HA]_{org}$	k_D	z	z/(1-z)
0.01	0.00242	0.00757	3.13	0.0331	0.0342
0.03	0.00497	0.02502	5.03	0.1093	0.1226
0.05	0.00686	0.04313	6.28	0.1883	0.2320
0.07	0.00884	0.06115	6.91	0.2670	0.3643
0.09	0.0091	0.0808	8.89	0.3532	0.4062

Table 4.7: Reactive Extraction of BA Using 10% TOA in Decanol at 313 K

[BA]	$[HA]_{aq}$	$[HA]_{org}$	k_D	z	z/(1-z)
0.01	0.00259	0.00749	2.31	0.03235	0.03343
0.03	0.00512	0.02488	4.71	0.1086	0.1219
0.05	0.0082	0.04184	5.21	0.1827	0.2235
0.07	0.0097	0.06031	5.86	0.2634	0.3075
0.09	0.0097	0.08	7.11	0.3494	0.3238

Table 4.8: Reactive Extraction of BA Using 10% TOA in 1-Decanol at 318 K

[BA]	$[HA]_{aq}$	$[HA]_{org}$	k_D	z	z/(1-z)
0.01	0.00326	0.0073	2.06	0.0293	0.0302
0.03	0.00611	0.02389	3.91	0.1043	0.1164
0.05	0.00907	0.0409	4.51	0.1787	0.2176
0.07	0.01411	0.0558	5.26	0.2440	0.3228
0.09	0.00126	0.077	6.11	0.3377	0.5098

Industrial scale fermenters used for the production of carboxylic acids usually operate in the temperature range of 305 to 313 K. Thus an extractant can be considered as effective only if it could operate efficiently in this temperature range. Generally, extraction is an exothermic process and with increase in temperature, the extractant efficiency decreases. However, it can be stated that the decrease in extraction is also a function of the extractant and diluent chosen i.e. the extracting medium. This decrease in k_D with increase in temperature can be attributed to the reversible complexation reactions between the organic acid and the amine. The complexation reactions in the organic phase involve a proton transfer reaction or hydrogen bond formation, and are mildly exothermic. The overall effect of temperature is attributed to the effects of different parameters such as the acid pKa, the amine-acid interaction, the solubility of the acid in both phases, the extractant basicity, and water coextraction.

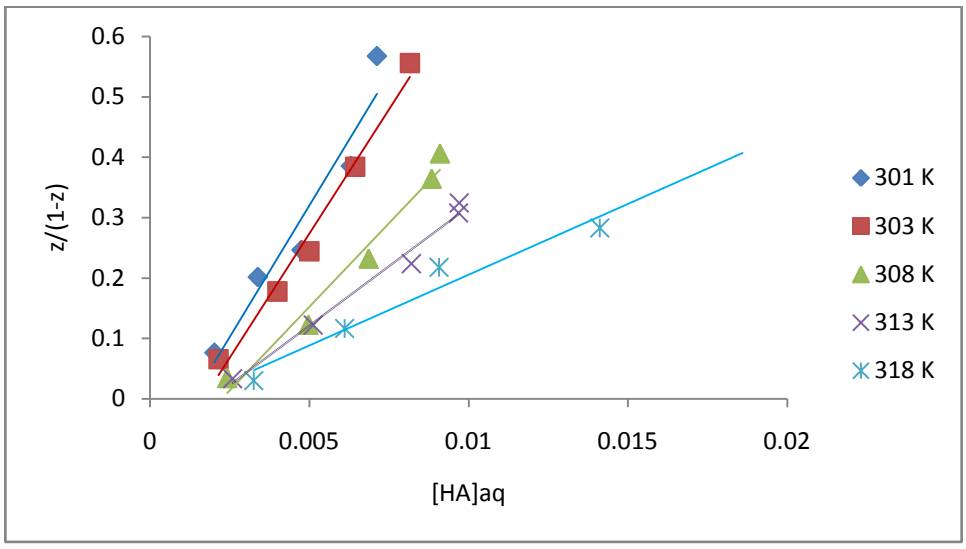

Figure 4.7: $[HA]_{aq}$ vs z/(1-z) for temperature ranging from 301K to 318K

The loading values are less than 0.5 for every case. It indicates the formation of 1:1 complex by the butyric acid and TOA. The extraction of carboxylic acids by extractant occurs by intermolecular hydrogen bonding or ion exchange of the extractant group with the acid. Extractions involving loading ratios less than 0.5, forms (1:1) complexes and the following Equation holds :

$$\frac{z}{1-z} = K_{E(1:1)} * [HA]_{aq} \qquad (14)$$

Slope of above graph yields equilibrium complexation constants as 65.93, 59.09, 43.90, 30.07, 29.50 at 301K, 303K, 308K, 313K, 318K respectively.

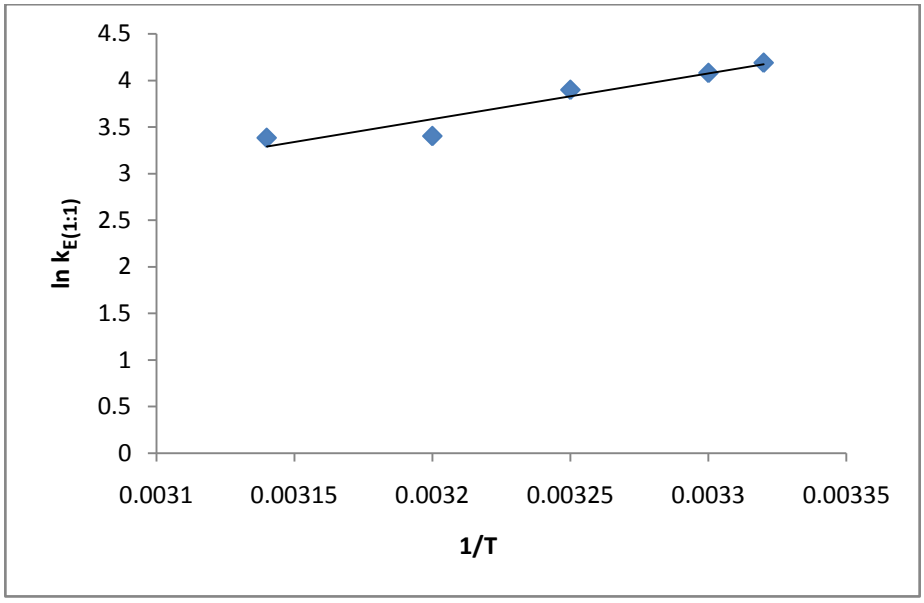

Figure 4.8: ln k_E vs 1/T for temperature ranging from 301to 318 K

If the enthalpy and entropy of reaction are assumed to be constant over the temperature range, the equilibrium complexation constant is related to temperature by the following equation:

$$\ln(k_E) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (15)$$

The above expression indicates that a plot of ln k_E vs 1/T should give a straight line. The slope is proportional to the enthalpy of reaction (ΔH), and the intercept is proportional to the entropy (ΔS). Slope of the above graph yields Enthalpy ΔH= -40.772 KJ/mol K and Entropy ΔS= −100.68J/molK. The extraction of carboxylic acids by extractant occurs by intermolecular hydrogen bonding or ion exchange of the extractant group with the acid. The extraction of Butyric acid by extractant-acid complexation is expected to be exothermic and to make the system more ordered. This increase in order means that a decrease in entropy is expected for the reaction. Further, the system becomes more ordered if the interaction between the acid and the extractant is strong.

CHAPTER: 5
CONCLUSIONS

5. Conclusions

The present research work of "Reactive Extraction of Butyric Acid (BA) using Tri-Octyl Amine (TOA) in 1-Decanol" deals with the important aspects of effect of pH, temperature and stirring.

From the equilibrium study the following conclusions can be drawn:

- Results show that with increase in pH, distribution coefficient decreases. At a pH of 1.41, distribution coefficient of 24 and extraction efficiency of 96 % was obtained.

- At a pH of 1.41, loading ratio of 0.8384 was obtained. Higher value of loading ratio (z) indicated the presence of 2:1 complex.

- For extraction using 10% TOA, initially as pH is increased from 1.41 to 2.29, there is gradual decrease in extraction and at higher pH greater than 4, very low k_D was obtained. Thus at pH > pKa of the acid, extraction is very low.

- Extraction efficiency has decreased from 96% to 82.99%. The reason being that with increase in pH, fraction of dissociated forms increases over the undissociated forms and hence tertiary amine perform poorly in neutral and basic media.

- For the physical extraction of butyric acid using decanol alone, highest distribution coefficient of 0.234 was obtained at a pH of 1.41 for 0.2M aqueous butyric acid solution. Whereas the highest distribution coefficient value of about 24 was obtained for the same butyric acid concentration of 0.2M, at pH of 1.41 when tri-ocyl amine was used in addition to 1-decanol.This shows that the chemical extraction is very much efficient than physical extraction. Also with increase in pH, no significant change was observed in the values of distribution coefficient.

- The distribution coefficients and extraction efficiencies were evaluated for concentration of butyric acid ranging from 0.01 to 0.09M and temperature ranging from 301K to 318K.

- The loading values are less than 0.5 for every case. It indicates the formation of 1:1 complex by the butyric acid and TOA. The extraction of carboxylic acids by

extractant occurs by intermolecular hydrogen bonding or ion exchange of the extractant group with the acid.

- We concluded that with increase in temperature, distribution coefficient decreases. Generally, extraction is an exothermic process and with increase in temperature, the extractant efficiency decreases.

- Plot of ln k_E vs 1/T yields a graph whose slope is proportional to the enthalpy of reaction (ΔH), and the intercept is proportional to the entropy (ΔS). Slope of the graph yields Enthalpy ΔH= -40.772 KJ/mol K and Entropy ΔS=-100.68J/molK.

- The use of active diluent, 1-decanol has also played an important role in the improvement of the distribution coefficient and extraction efficiency. Active diluents have functional groups that enable a greater solvation of the acid-amine complex. The solvent polarity controls the structure of the interfacial compounds formed by reaction between butyric acid and TOA.

CHAPTER: 6
FUTURE SCOPE

6. Future Scope

The present work on "Reactive Extraction of Butyric Acid (BA) using Tri-Octyl Amine (TOA) in 1-Decanol" deals with the important aspects of pH, temperature and stirring. However some scopes have remained which needs further attention.

- Addition of salts such as NaCl increases the distribution coefficient significantly. Distribution coefficients were found to be higher than the distribution coefficients found from no salt condition. Thus it is important to study the salting out effect within the solubility limits of NaCl. NaCl is not distributed equally between the the aqueous phase and the organic phase.

- Diluent in the presence of NaCl may and may not appear to be a good solvent for extracting the acid from the aqueous solution. For instance 1-butanolin presence of dissolved NaCl appears to be a good solvent to extract propionic acid from the aqueous solution, in view of the high values of distribution coefficient and selectivities.

- Hence, it is very important to study the effect of salts such as Na_2SO_4, NaCl on the reactive extraction process for a particular acid-extractant-diluent system.

- Here, active diluent is used for the present study. One can also study the effect of inactive diluents like toluene and determine the various parameters of reactive extraction.

REFERENCES

References

1) Aharon M. Eyal and Riki Canari, (1995) "pH Dependence of Carboxylic and Mineral Acid Extraction by Amine-Based Extractants: Effects of PKa, Amine Basicity, and Diluent Properties", *Ind. Eng. Chem. Res.*,34, 1789-1798

2) A. Keshav, K. L. Wasewar, and S. Chand, (2008) "Extraction of Propionic Acid Using Different Extractants (Tri-*n*-butylphosphate, Tri-*n*-octylamine, and Aliquat 336)" , *Ind. Eng. Chem. Res*., 47, 6192–6196

3) A. Keshav, K. L. Wasewar, and S. Chand, (2009) *"*Equilibrium and kinetics of reactive extraction of propionic acid using aliquat 336 and tri-n-butyl phosphate in n-hexanol", *Int. J. Chem. Reactor Eng*., vol. 7, pp. A35.

4) A. Keshav, K. L. Wasewar, and S. Chand, (2009) *"*Recovery of propionic acid by reactive extraction 1. Equilibrium; effect of pH and temperature; water co-extraction*",* *Desal. Water Treat*, vol. 3, pp. 91-98.

5) A. Keshav, K. L. Wasewar, and S. Chand, (2009)*"*Extraction of propionic acid from model solutions: effect of pH, salts, substrate, and temperature*,"AIChE J*., vol. 55, pp. 1705-1711.

6) Choudhury, B Basha and Swaminathan T, (1998) "Study of lactic Acid Extraction with Higher Molecular Weight Aliphatic Amines", *J. Chem. Technol. Biotechnol.*, 72, 111-116.

7) C.H. Zhang, H. Yang, F.X. Yang, Y.J. Ma, (2009) "Current progress on butyric acid production by fermentation*",* *Curr. Microbiol.,* 59 656–663.

8) D. C. Caval, L.A. Kloetzer, and A.I. Galaction, (2011) "Influence of Organic Phase Polarity on Interfacial Mechanism and Efficiency of Reactive Extraction of Acetic Acid with Tri-n-octylamine", *J. Chem. Eng. Data* , 56, 2521–2526.

9) E.Kahya, E.Bayraktar, U.Mehmeto_glu, (2001) "Optimization of Process Parameters for Reactive Lactic Acid Extraction", *Turk J Chem* 25, 223 -230.

10) Hasan Uslu, Cuma Bayat, Selahattin Gokmen, and Yavuz Yorulmaz, (2009) "Reactive Extraction of Formic Acid by Amberlite LA-2 Extractant ", *J. Chem. Eng. Data*, 54, 48–53.

11) Hasan Uslu and S İsmail Kırbaşlar , (2013) "Effect of Temperature and Initial Acid Concentration on the Reactive Extraction of Carboxylic Acids", *J. Chem. Eng. Data*, 58, 1822−1826

12) Y. S. Jun, E. Z. Lee, Y. S. Huh, (2007) "Kinetic study for the extraction of succinic acid with TOA in fermentation broth; Effects of pH, salt and contaminated acid", *Biochem. Eng. J*., 36, 8–13.

13) J. Zigová, E. Šturdik, D. Vandák, Š. Schlosser, (1999) "Butyric acid production by Clostridium butyricum with integrated extraction and pertraction*", Process Biochem.* 34 835–843.

14) Kertes A. S., King C. J., (1986) "Extraction chemistry of fermentation product carboxylic acids", *Biotechnol. Bioeng*, 28, 269-282.

15) Keshav, A., Wasewar, K. L., and Chand, S. (2008), "Reactive extraction of propionic acidwith tri-n-octylamine in different diluents", *Sep. Purif. Technol*., 63, 179–183.

16) King, C. J., and Tamada, J. A. (1990). Extraction of carboxylic acids with amine extractants:Effect of temperature, water coextraction, and process considerations, *Ind. Eng. Chem.Res.*, 29, 1327–1333.

17) K.L.Wasewar, A.B.M. Heesink, G.F. Versteeg and V.G. Pangarkar, (2006) *"*Equilibria and kinetics for reactive extraction of lactic acid using Alamine 336 in decanol*", J. Chem. Tech. Biotechnol*. 77 1068-1075.

18) Małgorzata djas, marek henczka, (2012) "Influence of mixing on the course of reactive Extraction of carboxylic acidsUsing supercritical carbon dioxide**"** *European Conference on Mixing Warsaw*.

19) M. Dwidar, J.Y. Park, R.J. Mitchell, B.I. Sang, (2012) "The future of butyric acid in industry*". Sci. World J.*.

20) M.N. Ingale, V.V. Mahajani, (1994) *"*Recovery of butyric-acid, valeric acid, and caproic acid (BVC acids) from an aqueous waste stream using tributylphosphate (TBP) as an extractant*", Sep. Technol.* 4 252–257.

21) M.N. Ingale, V.V. Mahajani, (1996) "Recovery of carboxylic acids, C2-C6 from an aqueous waste stream using tributylphosphate(TBP) : Effect of presence of inorganic acids and their sodium salts", Sep. Technol. 6 1-7

22) R. G Robinson, D. Y Cha, (1986) "Controlled pH Extraction in the Separation of Weak Acids and Bases", *Biotechnol. Prog.* (1), 18.

23) Shang-Tian Yang, Scott A. White, and Sheng-Tsiung Hsu, (1991) "Extraction of Carboxylic Acids with Tertiary and Quaternary Amines: Effect of pH", *Ind. Eng. Chem.* Res., 30, 1335-1342.

24) Sushil Kumar, Suantak Kamsonlian, and Neha Chomal, (2014) "Equilibrium Study on Reactive Extraction of Nicotinic Acid from Aqueous Solution", *International Journal of Chemical Engineering and Applications*, Vol. 5, No. 6.

25) Yang, White, S.A. and Hsu, S.T, (1991) "Extraction of Carboxylic Acids with Tertiary and Quaternary Amines: Effect of pH", *Ind. Eng. Chem. Res.*, 30, 1335-1342.

26) Yeon Ki Hong, Won Hi Hong, and Dong Hoon Han, (2001) "Application of Reactive Extraction to Recovery of Carboxylic Acids", *Biotechnol. Bioprocess Eng.*, 6: 386-394.

27) Z.T. Wu and S.T. Yang, (2003) "Extractive fermentation for butyric acid production from glucose by Clostridium tyrobutyricum", *Biotechnology Bioengineering* 82 93–102.